Bio-oil and bio-char production from corn cobs and stover by fast pyrolysis ☆

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ABSTRACT

Bio-oil and bio-char were produced from corn cobs and corn stover (stalks, leaves and husks) by fast pyrolysis using a pilot scale fluidized bed reactor. Yields of 60% (mass/mass) bio-oil (high heating values are $\sim$20 MJ kg^{-1}, and densities >1.0 Mg m^{-3}) were realized from both corn cobs and from corn stover. The high energy density of bio-oil, $\sim$20–32 times on a per unit volume basis over the raw corn residues, offers potentially significant savings in transportation costs particularly for a distributed "farm scale" bio-refinery system. Bio-char yield was 18.9% and 17.0% (mass/mass) from corn cobs and corn stover, respectively. Deploying the bio-char co-product, which contains most of the nutrient minerals from the corn residues, as well as a significant amount of carbon, to the land can enhance soil quality, sequester carbon, and alleviate environmental problems associated with removal of crop residues from fields.

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1. Introduction

Owing to economies of scale associated with higher production costs, it has been established that the optimum size for a cellulosic bio-fuels plant is four to five times larger than is the optimum grain to ethanol plant, depending on the type of conversion [1]. These centralized, large biomass processing plants will process up to 23,000 tonnes of biomass per day, creating serious transportation and biomass storage and handling problems and high expenses [2]. These studies have also found that for production of Fischer–Tropsch liquids, distributed "farm scale" fast pyrolysis units for production of high density bio-oil as an intermediate product to be gasified at the central plant can decrease the transportation costs. The transportation cost savings are enough to offset the higher operational costs and biomass costs. Additionally, the study found that the distributed pyrolysis model shields the operation from variations in delivery costs and crop yields as the overall processing costs have low sensitivity to these factors [2]. Presumably, these positive economic factors would

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generally apply to any liquid fuel production from lignocellulosic biomass that uses fast pyrolysis liquids as an intermediate product.

At 23 Mt y^{-1}, corn stover is by far the largest quantity of agricultural crop biomass produced in the United States [3,4]. Therefore, it is often targeted as a potential feedstock for cellulosic bio-fuels production. However, harvesting of corn stover from fields can have negative environmental and soil quality repercussions, including decreases in soil organic carbon, depletion of plant nutrients, decreases in the soil's ability to retain plant nutrients and plant available water, and increases in water runoff and soil erosion [3]. Therefore more fertilizer and irrigation water would be required to continue the same levels of crop production. Also surrounding water quality would deteriorate due to increased sediment and agricultural chemicals in surface runoff for fields from which crop residues were removed. Lal [5] has reported that removal of as little as 25% of corn stover from some soils can have major detrimental effects.

One potential solution suggested for these environmental concerns is the application of the bio-char co-product of fast pyrolysis to soils [6]. Soil application of bio-char may enhance both soil quality and can be an effective means of sequestering large amounts of C, thereby helping to mitigate global climate change through C sequestration [6,7]. Use of bio-char as a soil amendment will offset many of the problems associated with removing crop residues from the land. Bio-char is highly absorbent and therefore increases the soils, ability to retain water, nutrients and agricultural chemicals, preventing water contamination and soil erosion. It also contains most of the nutrients that were in the biomass, can release them slowly, and is a liming agent [7]. Additionally, the carbon in bio-char applied to soil will be removed from the atmosphere and may remain sequestered in the soil for thousands of years [6,7], making the fast pyrolysis an overall carbon negative process.

In this work we have performed the fast pyrolysis of two corn residues, corn cobs and corn stover (defined for this work as stalks, leaves and husks with no cobs) for bio-oil and bio-char production in a fluidized bed reactor and characterized these products for energy and soil amendment properties.

2. Methods

2.1. Pyrolysis

Pyrolysis was carried out in a bubbling fluidized bed of quartz sand at temperatures of about 500 °C. The apparatus, described previously by Boateng et al. [8,9] includes a 7.62 cm (3 in) diameter fluidized reactor section, 2 cyclones in series for bio-char separation followed by a series of 4 condensing canisters cooled by circulating water jackets maintained at about 4 °C and a series of three electrostatic precipitators that collect the largest fraction of the pyrolysis oil produced. The actual feed rates varied between 1.0 and 1.6 kg h^{-1}. The functions of each of the components are described in detail by Boateng et al. [8]. Temperature and pressure measurements were carried out using thermocouples and pressure transducers and logged using a Labview data acquisition and control system (National

Instruments, Austin, TX). Mass recovery was carried out by gravimetric analysis of the feedstock material used versus the materials produced including bio-oil and bio-char. The uncondensed gas composition was analyzed by gas chromatography (GC) (Agilent MicroGC 3000A). Gas quantity was determined by the difference between the fluidizing gas measured by mass flow meter (Alicat Scientific, Tucson, AZ) and the effluent gas measured with a bulk gas flow meter (Metris).

2.2. Feedstock characterization

Proximate and Ultimate Analysis, Heat of Combustion and XRF mineral analysis of the corn cob and corn stover feedstocks were done by Wyoming Analytical Laboratories, Inc. (Laramie, WY). Component analysis on the feedstock was done by Dairy One, Inc. (Ithaca, NY). SEM Microscopy was performed as described below.

2.3. Product characterization

Bio-oil water content was determined by Karl-Fischer (K-F) titration using 3:1 methanol:chloroform as solvent. GC/MS analysis of bio-oil was performed on an Agilent 6890N GC equipped with an Agilent 5973 mass selective detector (MSD). The GC column used was a DB-1701 60 m × 0.25 mm, 0.25 μm film thickness. The oven was programmed to hold at 45 °C for 4 min, ramp at 3 °C min^{-1} to 280 °C and hold at 280 °C for 20 min. The injector temperature was 250 °C, and the injector split ratio was set at 30:1. The flow rate was 1 cm^3 min^{-1} of the He carrier gas. The bio-oil samples were prepared as ~6% solutions in acetone which were filtered through 0.45 μm PTFE filters prior to injection. For quantification, response factors relative to the internal standard, fluroanthene, were determined for each quantified component following Oasmaa [10].

HPLC analysis of the bio-oils was performed on a Waters Breeze HPLC system using a refractive index detector, set at 30 °C. The isocratic mobile phase was 0.007 N H$_3$PO$_4$. The column used was an Aminex HPX-87H, 300 × 7.8 mm (Bio-Rad, Inc.), and was heated to 30 °C. The pump was programmed at a flow rate 0.6 cm^3 min^{-1} and n-propanol was used as the internal standard for quantification [10].

Elemental analysis and physical property determination for bio-oil was done by Galbraith Laboratories, Inc. (Knoxville, TN). Bio-char analysis and XRF elemental analysis was done by Wyoming Analytical Laboratories, Inc. (Laramie, WY).

SEM Microscopy was performed as follows: bio-char samples (powders) were transferred from storage vials to Petri dishes and dispersed separately by agitation into a thin layer. For each sample, one side of a 25 mm dia. conductive carbon adhesive tab (Electron Microscopy Sciences, Hatfield, PA) was gently applied to the sample layer, then the opposite side of the tab was glued with Duco cement (ITW Performance Polymers, Riviera, FL) to a standard glass microscope slide. After drying the cement, each sample was sputtered with a thin layer of gold and examined with a model Quanta 200 FEG scanning electron microscope (FEI Co., Inc., Hillsboro, OR), operated in the high vacuum, using secondary electron imaging mode.

Surface area measurements on bio-char were obtained from nitrogen adsorption isotherms at 77 °K using a Nova 2000 Surface Area Analyzer (Quantachrome Corp., Boynton Beach,

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                Corn Cobs

        C 47.35% (wt)
        H 5.90%
        N 0.69%
        S 0.18%
        O 38.07%
        Ash 1.94%

        HHV 17.8 MJ kg⁻¹
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              Pyrolyzer
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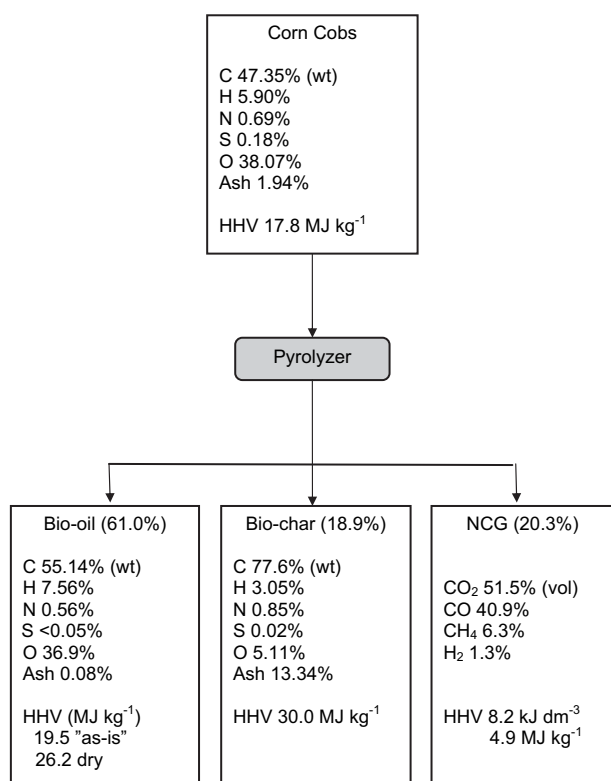| Bio-oil (61.0%)	Bio-char (18.9%)	NCG (20.3%)
C 55.14% (wt) H 7.56% N 0.56% S <0.05% O 36.9% Ash 0.08% HHV (MJ kg⁻¹) 19.5 "as-is" 26.2 dry	C 77.6% (wt) H 3.05% N 0.85% S 0.02% O 5.11% Ash 13.34% HHV 30.0 MJ kg⁻¹	CO_2 51.5% (vol) CO 40.9% CH_4 6.3% H_2 1.3% HHV 8.2 kJ dm⁻³ 4.9 MJ kg⁻¹

Fig. 1 – Elemental analysis (dry basis) and high heating value (wet basis) of corn cob and its pyrolysis products (average of two pyrolysis experiments).

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                Corn Stover

        C 46.60% (wt)
        H 4.99%
        N 0.79%
        S 0.22%
        O 40.05%
        Ash 4.88%

        HHV 18.3 MJ kg⁻¹
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              Pyrolyzer
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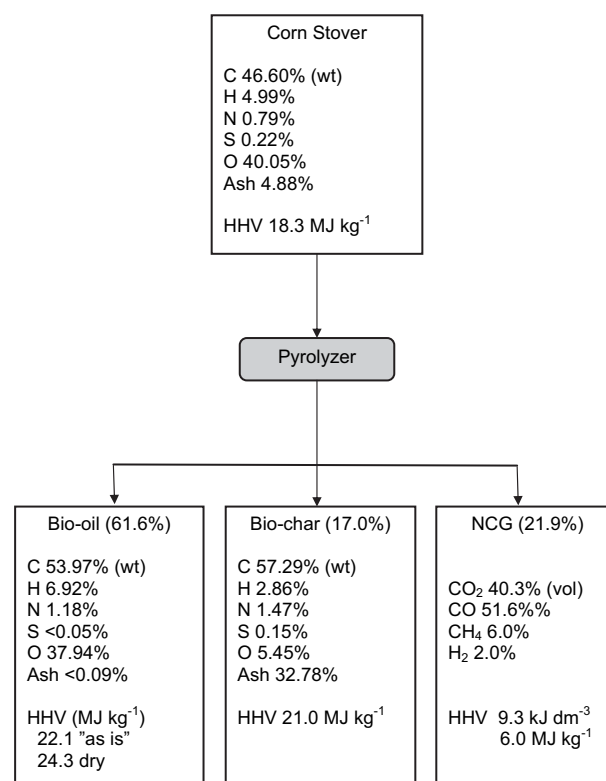| Bio-oil (61.6%)	Bio-char (17.0%)	NCG (21.9%)
C 53.97% (wt) H 6.92% N 1.18% S <0.05% O 37.94% Ash <0.09% HHV (MJ kg⁻¹) 22.1 "as is" 24.3 dry	C 57.29% (wt) H 2.86% N 1.47% S 0.15% O 5.45% Ash 32.78% HHV 21.0 MJ kg⁻¹	CO_2 40.3% (vol) CO 51.6%% CH_4 6.0% H_2 2.0% HHV 9.3 kJ dm⁻³ 6.0 MJ kg⁻¹

Fig. 2 – Elemental analysis (dry basis) and high heating value (wet basis) of corn stover and its pyrolysis products (average of two pyrolysis experiments).

FL). Specific surface areas (S_{BET}) were determined from adsorption isotherms using the Brunauer, Emmett, and Teller (BET) equation. A Thermo Orion pH meter (Beverly, MA) was used to measure pH, where 0.5 g of sample was placed in 50 cm^3 of deionized water, covered with parafilm, and allowed to equilibrate by stirring at 300 rpm for 72 h. Bio-chars were heated to 650 °C under a flow of air at 1.07 dm^3 min^{-1} for 6 h increments until there was no change in weight. Ash was calculated as a percentage of initial bio-char dry weight. Average particle size distribution was measured for the bio-char samples by a Coulter LS™ Instrument (Miami, FL) which uses a light scattering technique. Particle size distribution followed a bell shape curve and average particle size (in μm) was selected as the value that best represented each sample size distribution. For the test, approximately 100 mg of bio-char were dispersed in water.

Determination of metal ion adsorption by bio-char was performed as follows. Copper chloride (II) and nitrates of nickel (II) and zinc (II) were obtained from Fisher Scientific (Fair Lawn, NJ). Cadmium nitrate (II) was obtained from EM Science (Cherry Hill, NJ). Single 1 mmol dm^{-3} metal ion solutions were made in a 0.07 mol dm^{-3} sodium acetate – 0.03 mol dm^{-3} acetic acid buffer, pH 4.8. For equilibrium measurements, 0.25 g of bio-char was added to 25 cm^3 of the metal solution in 150 cm^3 beakers. The pH of the slurry was recorded at the beginning and at the end of the experiment. Beakers were covered with Par-afilm and the slurry was stirred with Teflon coated, magnetic stir-bars for 24 h at 300 rpm using a multiple stirrer, VarioMAC Multipoint HP 15 (H + P Labortechnik GmbH, Germany). An aliquot of the suspension was collected using a disposable syringe and filtered through a 0.22 μm Millipore filter (Millipore Corp., Bedford, MA) to remove any carbon particles. The sample was diluted to 1:100 by volume with 4 vol% HNO_3 (Ultrapure, ICP grade) and analyzed by inductively coupled plasma, ICP spectroscopy using a Leeman Labs Profile ICP–AES (Leeman Labs, Hudson, NH).

Table 1 – Inorganic elemental composition of pyrolysis feedstock determined by XRF (g kg⁻¹).

	Corn cobs	Corn stover
Si	5.33	27.9
Al	0.18	5.09
Fe	0.08	2.35
Ca	0.23	3.25
Mg	0.55	2.34
Na	0.10	0.23
K	10.38	4.44
Ti	0.003	0.37
Mn	0.01	0.98
P	1.11	2.15
Ba	0.11	0.02
Sr	0.002	0.005
S (Inorganic)	0.14	0.05

Table 2 – Chemical analysis of the feedstock.

	(%, dry matter)					
	Total cell wall[a]	Cellulose[b]	Hemicellulose[c]	Lignin	NFC	Crude protein
Corn cobs	71	30	38	3	24	4
Corn stover	82	48	29	6	5	6

a Total cell wall measured as Neutral Detergent Fiber (NDF).
b Cellulose measure as NDF – lignin.
c Hemicellulose measured as NDF – Acid Detergent Fiber (ADF).

3.   Results and discussion

3.1.   Feedstock analysis

Moisture contents of the feedstocks for the pyrolysis experiments were 6.8% for the corn cobs and 2.5% for the stover. The elemental analysis of the organic material in the two feedstocks was similar (Figs. 1 and 2). XRF analysis of the ash indicated that K (1.0 wt%) was the most abundant element in the inorganic fraction of the corn cobs and Si (2.8 wt%) was the most abundant in the corn stover (Table 1). Phosphorous levels were similar at about 0.2% for each feedstock. Other important mineral elements including Ca and Mg were more highly concentrated in the corn stover.

Component analysis of the corn crop residues is presented in Table 2. Overall cell wall material was measured as neutral detergent fiber. Lignin was measured as 3.3% of the dry material for corn cobs and 6.3% for corn stover. Most literature on corn crop reside composition have reported higher lignin contents than these [11–13]. Cellulose, which we estimated as the difference between acid detergent fiber and lignin was 29.8% of the corn cobs and 47.5% of the corn stover. Hemicellulose, estimated as the difference of neutral detergent fiber and acid detergent fiber was 38.3% of the corn cobs and 28.6% of the corn stover. Non-fiber carbohydrates (NFC), comprising non-cell wall materials such as starch, sugar and pectin were 23.7 and 5.3% for the corn cob and corn stover respectively.

The gross heating value of the two corn crop residues was similar, with corn cobs having an HHV of 17.8 MJ kg^{-1} and corn stover at 18.3 MJ kg^{-1} (Figs. 1 and 2). Assuming a bulk density of 40–80 kg m^{-3} (for corn stover, [14]), the energy density is estimated as 0.7–1.4 GJ m^{-3} for the corn crop residues.

3.2.   Pyrolysis products distribution

Actual recovery of bio-oil averaged 41% of the feedstock for corn cobs and 58% for the corn stover (Table 3). Bio-char yields were in 19% and 17% yield, while the NCG produced measured 15% and 5% respectively. Due to the small size of the experiments, 26% (cobs) and 19% (stover) of the biomass remained in the tubing and piping of the system and was not physically recovered. Therefore true estimates were established by mass and elemental balance (Fig. 3) using an optimization model. The corrected bio-oil yields (wet basis) therefore averaged 61% for corn cobs and 62% for corn stover and the corrected bio-char yields were 19% and 17% while the NCG yields are to 20% and 22% respectively. In Fig. 3 we also show details on the distribution of elements through the pyrolysis products, particularly carbon balance. Distribution of carbon is especially important in developing renewable fuels. The bio-oil products contained 55–62% of the feedstock carbon, 20–30% was found in bio-char and the remaining 15–18% was found in the NCG.
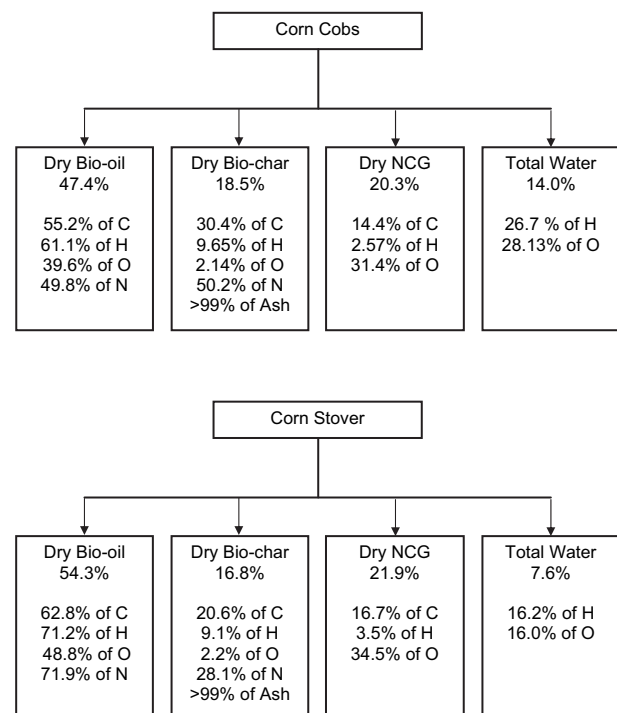

Fig. 3 – Mass and elemental balance (all values for feedstock are 100%) for pyrolysis of corn cobs (top) and corn stover (bottom).

Table 3 – Pyrolysis product distributions.[a]

	Corn cobs		Corn stover	
	Recovery	Corrected[b]	Recovery	Corrected[b]
Bio-oil	40.9%	61.0%	58.2%	61.7%
Bio-char	18.9%	18.9%	17.1%	17.0%
Non-condensable gas	14.7%	20.3%	5.3%	21.9%

a Average of two pyrolysis experiments for each feedstock.
b Corrected yields estimated from mass elemental balance using analysis of the feedstock and products (Figs. 1 and 2).

Table 4 – Quantification of some bio-oil components.[a]

Method	Compound	Corn cob bio-oil			Corn stover bio-oil		
		Condensers 1–4	ESP	Whole oil[b]	Condensers 1–4	ESP	Whole oil[b]
K-F[c]	Water (wt% of bio-oil)	37.68	11.27	24.83	15.54	5.94	9.15
Cellulose/hemicellulose derived compounds (wt% of bio-oil)							
HPLC	Levoglucosan	6.91	3.63	5.31	14.75	11.33	12.36
HPLC	Hydroxyacetaldehyde	0.86	2.05	1.44	4.03	3.99	4.00
HPLC	Acetic acid	6.44	6.42	6.43	7.56	6.20	6.26
HPLC	Acetol	10.38	9.89	10.14	8.58	6.40	7.08
GC	Furfural	0.89	1.53	1.20	0.60	0.79	0.71
GC	Furfuryl alcohol	0.24	0.36	0.30	0.14	–	0.04
GC	3-Methyl-2-cyclopenten-1-one	0.26	0.51	0.38	0.08	0.09	0.09
GC	4-Hydroxy-4-methyl-2-pentanone	0.08	0.17	0.12	0.07	0.13	0.11
Lignin-derived compounds (wt% of bio-oil)							
GC	Phenol	0.64	0.96	0.79	0.13	0.33	0.30
GC	o-Cresol	0.15	0.22	0.17	0.08	0.12	0.10
GC	p-Cresol	0.15	0.22	0.19	0.05	0.13	0.12
GC	m-Cresol	0.13	0.15	0.17	0.03	0.03	0.03
GC	2,4-Dimethyl phenol	0.05	0.04	0.05	–	–	–
GC	3,5-Dimethylphenol	0.03	0.38	0.02	–	–	–
GC	4-Ethyl phenol	0.37	0.33	0.54	0.17	0.25	0.22
GC	3-Ethylphenol	0.03	–	0.02	–	–	–
GC	2-Ethylphenol	0.02	–	0.01	–	–	–
GC	Guaiacol	0.44	0.78	0.61	0.19	0.29	0.25
GC	2-Methoxy-4-methyl phenol	0.37	0.25	0.31	0.22	0.15	0.17
GC	Isoeugenol	0.22	0.35	0.28	0.14	1.26	0.82
GC	2,6-Dimethoxyphenol	0.41	0.84	0.63	0.24	0.46	0.38

a Average from two pyrolysis runs for each feedstock.
b Whole bio-oil percentages based on a weighted sum of the condenser and ESP bio-oils.
c K-F: Karl-Fischer Titration.

3.3. Bio-oil characterization

As mentioned earlier, liquid product was collected in a series of four condensers, each jacketed with flowing cold water (∼4 °C) followed by three electrostatic precipitators (ESP) in series, where the largest fraction of bio-oil is collected. The ESP captured 49 wt% of corn cob bio-oil and 66 wt% corn stover bio-oil. More water was collected in the condenser fractions than at the ESPs (Table 4). Overall water content was 25.3% for bio-oil from corn cobs and 9.2 wt% for corn stover. Typically bio-oil from hardwood contains 15–30 wt% water.

The dry basis elemental analysis of the bio-oils is shown in Figs. 1 and 2. The bio-oil C:O ratios were higher in the bio-oil than in the feedstocks because pyrolysis partitions O into the NCG primarily as CO_2 and CO, along with the production of water. Also, the corn cob bio-oil had a slightly higher C:O ratio than did the corn stover bio-oil. As a result the high heating value (HHV) was slightly higher for bio-oil from corn cobs on a dry basis, 26.2 MJ kg^{-1} while the corn stover bio-oil had a dry basis HHV of 24.3 MJ kg^{-1}. However, due to the high water content of the corn cob bio-oil its "as-is" HHV is lower than that of the corn stover bio-oil, 19.5 MJ kg^{-1} and 22.1 MJ kg^{-1} respectively.

The bio-oils are denser than water, 1.1770 g cm^{-3} and 1.2451 g cm^{-3} for bio-oil from corn cobs and corn stover, respectively. Using these densities and HHV values reported above, the bio-oils would contain 23–27.5 MJ dm^{-3} ("as-is" basis) compared with 32 MJ dm^{-3} for gasoline. When compared with above mentioned energy density for the biomass, the bio-oils

have 20–32 times greater energy content per unit volume making transportation of bio-oil much more efficient and cost effective than transportation of the corn residues. These transportation cost savings can provide the impetus for a bio-refinery model based on distributed small scale pyrolysis units which produce bio-oil for shipping to a centralized location where transportation fuels and co-products would be produced [2].

Some individual chemical compounds found in the bio-oils are quantified in Table 4. The compounds most abundant in the bio-oils (other than water) were small water soluble oxygenated

Table 5 – Minerals contained in bio-char co-product (g kg^{-1}).

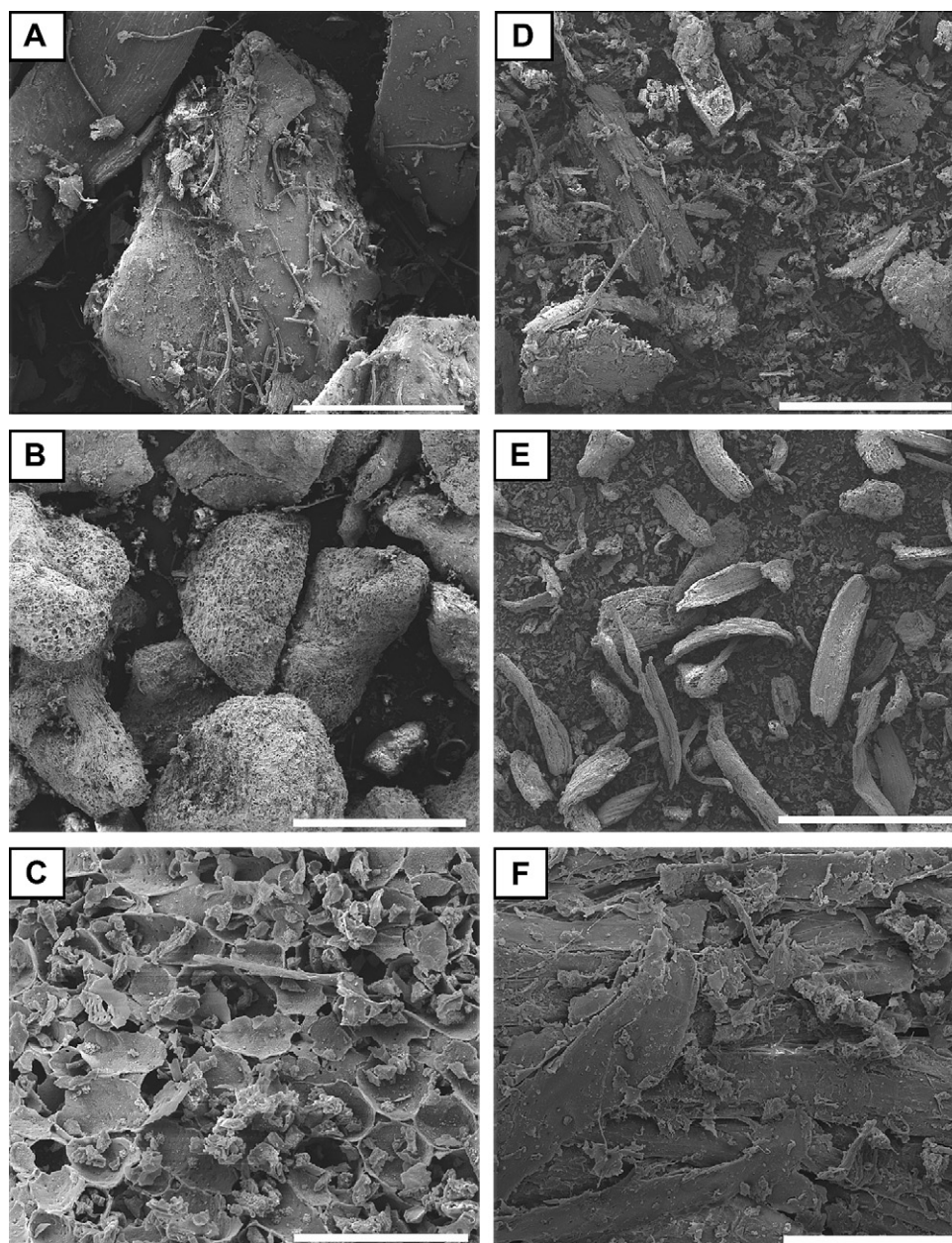|	Corn cobs	Corn stover
Si	73.50	196.23
Al	0.21	33.10
Fe	0.65	15.95
Ca	0.97	20.13
Mg	2.15	14.24
Na	0.07	01.07
K	43.35	23.46
Ti	0.01	02.39
Mn	0.05	0.65
P	4.36	12.94
Ba	0.00	0.06
Sr	0.03	0.16
S (Inorganic)	0.50	3.24

Fig. 4 – SEM photographs of A. corn cobs, bar = 1 mm, B. corn cob bio-char, bar = 1 mm, C. corn cob bio-char, bar = 100 μm, D. corn stover, bar = 1 mm, E. corn stover bio-char, bar = 1 mm and F. corn stover, bar = 100 μm.

molecules derived from the polysaccharides in the corn crop residues. The most abundant compounds in this class are levoglucosan, hydroxyacetaldehyde, acetol and acetic acid. Most of these compounds were found in slightly higher concentrations in the bio-oils collected at the condensers than at the ESPs. Compounds derived directly from cellulose including levoglucosan and hydroxyacetaldehyde [15] were generally found in higher concentration in bio-oils from corn stover, reflective of the higher concentration of cellulose in that feedstock.

Decomposition of the lignin found in biomass results in production of numerous water insoluble phenolic compounds, both GC observable lignin monomer derivatives and higher molecular weight lignin oligomers [16,17]. The most abundant lignin-derived small molecule in the corn cobs bio-oil was phenol

(0.8 wt%) and the most abundant small phenolic compound in the bio-oils from corn stover was isoeugenol (0.8 wt%). The phenolic compounds were found in higher concentrations in bio-oils collected at the ESP than the bio-oils collected at the condensers.

Table 6 – Physical and chemical properties: pH, surface area (BET), and percent moisture content (MC) of corn cob and corn stover bio-chars.

	BET ($m^2\,g^{-1}$)	MC (%)	pH
Corn cob bio-char	0	11.1 ± 1.1	7.816
Corn stover bio-char	3.10 ± 0.26	8.8 ± 1.4	7.157

Table 7 – Particle size distribution of bio-chars (μm).							
	Mean	Std	<10%	<25%	<50%	<75%	<90%
Corn cob bio-char	708.8	513.3	71.58	265.5	651.3	1043	1479
Corn stover bio-char	373.6	420.9	30.35	93.69	212.3	477.8	1008

3.4. Bio-char characterization

As mentioned earlier, bio-char additions to soils may mitigate some of the detrimental effects of removing crop residues such as corn cobs and stover from fields and may actually enhance soil quality. Applying the bio-char to the soil replaces carbon, nitrogen and most of the plant nutrients that are removed from the soil with the biomass. Carbon in bio-char is highly stable in soil environments and may be sequestered for thousands of years [6,7]. The mass balance (Fig. 3) shows that 30% and 21% of the corn cobs' and corn stovers' carbon is found in the bio-char, and that nitrogen content was split between bio-oil and bio-char. Overall ash content of the bio-char was 13.1% for the corn cob bio-char and 32.4% for the corn stover bio-char, a difference reflective of the higher ash content of the corn stover feedstock. Important plant mineral nutrients such as K, P, Ca and Mg are concentrated in the ash (Table 5).

Physical and chemical properties of the corn cob and corn stover bio-chars were characterized. SEM images of both the feedstocks and the bio-char produced from them are shown in Fig. 4 and illustrate the large structural differences between the bio-chars from the two feedstocks. Bio-char pH was neutral to slightly alkaline (Table 6). Typical feedstocks for carbon production such as coal, wood and coconut shells produce more acidic carbons [18], however, chars made from plant or animal waste generally yield higher pH bio-chars that reflect the presence of ash (salts of base metals, Table 5) admixed with the bio-char. In soil environments, the bio-char will initially act as a liming agent raising the soil pH by dissolving the ash and releasing the base cations to the soil solution. Subsequent oxidation of the bio-char surfaces will create carboxylate groups such that the bio-char becomes a weak acid. Bio-chars produced at lower temperatures have higher yield recoveries, and contain more C=O and C–H functional groups that can serve as nutrient exchange sites after oxidation [19].

Surface area as measured by N_2 adsorption was negligible for both bio-chars, 0 m^2 g^{-1} and 3.1 m^2 g^{-1} respectively for corn cob and corn stover bio-chars (Table 7). Mean particle size was 513 μm and 421 μm for corn cob and corn stover bio-chars, respectively with the corn stover bio-char presenting a broader range of sizes. Ninety percent of the particles were smaller than 1479 μm and 1008 μm for the corn cob and corn stover bio-chars, respectively. In soil environments, bio-chars with small particle size and high internal porosity are expected to contribute most to the enhancement of soil quality. Because of their relatively low surface areas and the coarse particle size distributions, these bio-chars may not be ideal for soil quality enhancement. On the other hand, the large particle size should enhance stability of the bio-char C in soil environments.

Another potential use for bio-char is metal adsorption. Four metal ions considered environmental pollutants and commonly found in both drinking and wastewater were chosen to test: Cu^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+}. Corn stover bio-chars removed more metal ions in general than corn cob chars (Table 8). Bio-chars were most effective at removing Cu from solution, followed by Zn, Cd and Ni. It is possible that the chars ability to remove metal ions is related to their surface properties rather than their surface area (porosity). For the corn cob and corn stover bio-chars, ash content was almost twice as high in the corn stover as it was in the corn cob bio-char (Figs. 1 and 2). Additionally, from Table 5 it is clear that corn stover bio-char contains significantly larger amounts of inorganic components that could be partially represented in the bio-char as surface charged species possibly leading to some chemisorption phenomena. Lima and Marshall [20] have postulated that phosphorous in the form of phosphate groups bridged with the carbon matrix of poultry manure-based carbons could aid in the carbon's ability to uptake positively charged metal ions. This can be the case, despite low surface area. The above results show that corn stover bio-char could possibly be used for remediation of positively charged metal ions, such as copper, cadmium and zinc.

An alternative use for fast pyrolysis bio-char to soil amendment or metal adsorption is use as a renewable solid fuel. The HHV value for bio-char from corn cobs (Figs. 1 and 2) was 30.0 MJ kg^{-1} and 21.0 MJ kg^{-1}, values comparable to some coals. Nitrogen levels in the bio-char were 0.5–1.5% and sulfur levels were 0.02–0.15% important information for predicting NO_x and SO_x emissions from combustion of the bio-chars.

3.5. Non-condensable gas

Composition of the NCG measured by in-line GC is shown in Figs. 1 and 2. The gas consisted mainly of CO and CO_2 with small amounts of CH_4 and H_2 present. The gas from the corn stover contained less non-combustible CO_2 making it a slightly higher quality fuel gas than that from the corn cobs. Calculated heats of combustion for the product gases (nitrogen free) were 8.2 kJ dm^{-3} (4.9 MJ kg^{-1}) and 9.3 kJ dm^{-3} (6.0 MJ kg^{-1}) for the corn cob and corn stover NCG respectively.

Table 8 – Amount of metal ion (mmol g^{-1}, dry) adsorbed by bio-char from a single metal solution (1 mmol dm^{-3}). Percent adsorption in parentheses.				
	Cu^{2+}	Cd^{2+}	Ni^{2+}	Zn^{2+}
Corn cob bio-char	0.030 (54.5)	0.021 (22.6)	0.013 (12.3)	0.022 (21.3)
Corn stover bio-char	0.045 (80.3)	0.029 (31.1)	0.031 (29.2)	0.038 (37.2)

Table 9 – Energy recovery.[a]		
	Corn cobs	Corn stover
Bio-oil	48.6%	54.5%
Bio-oil + bio-char	71.3%	68.7%
Bio-oil + bio-char + NCG	75.7%	74.0%

a Average of two runs per feedstock.

3.6. Energy recovery

Based on heats of combustion of the feedstocks and products, it was estimated that the bio-oil from corn crops contains 67% (cobs) and 74% (stover) of the feedstocks' energy. Of the overall input energy (biomass and heat), ~49% is recovered in the bio-oil for corn cobs and ~55% of the overall energy is recovered for the corn stover (Table 9). Bio-oil and bio-char constitute an energy efficiency of ~70% for both feedstocks. Total pyrolysis products give an overall energy efficiency of ~75% in both cases. The balance of the energy is attributed to reactor heat loss and energy lost in the condenser train. Total heat losses for this system were previously measured as ~18% of the total energy input [8], giving a total energy closure of ~93%.

4. Conclusions

Fast pyrolysis of corn cobs and corn stover (stalks, leaves and husks) was carried out in a pilot scale fluidized bed reactor. Bio-oil yield was ~60% from the corn crop residue feedstocks. Specific gravity of the bio-oils was greater than 1.0 and the HHV was about 20 MJ kg^{-1}; therefore, these bio-oils have 20–32 times the energy density of the biomass feedstocks on a volume basis, making transportation of bio-oil more cost effective than transportation of biomass. Bio-char yields were 17–19% on a mass basis. The bio-char is potentially a valuable soil amendment because it contains most of the mineral nutrients in the corn residues, is a good absorbent of nutrients and agricultural chemicals and may sequester C. Application of bio-char to the soil may solve several major environmental problems associated with of removal of corn crop residues from the field and thereby enhance the sustainability of biomass harvesting and bio-fuels production.

Acknowledgments

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